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Journal of Alloys and Compounds 444–445 (2007) 98–103

Journal of ALLOYS AND COMPOUNDS

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Connections between the Pu–Ga phase diagram in the Pu-rich region and the low temperature phase transformations

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Received 21 July 2006; received in revised form 2 September 2006; accepted 14 September 2006
Available online 13 November 2006

Abstract

Significant progress has been made in recent years regarding the equilibrium phase diagram of the Pu–Ga system. For decades, researchers outside of the former Soviet Union considered the δ phase in Pu–Ga alloys to be in the state of thermodynamic equilibrium down to low temperatures. Recently, decades of experimental work in Russia have been published that indicate the existence of a eutectoid decomposition of the metastable δ phase to α phase and Pu_3Ga. Phase diagram calculations by a number of researchers have predicted this eutectoid transformation as well. In this work, we review the experimental and calculated phase diagrams and also comment on the expected consequences of the IIIrd law of thermodynamics with respect to the form of the delta phase field. Assembled data from the literature on the martensite start (M_S) and reversion (R_S) temperatures for the $\delta \rightarrow \alpha'$ transformation as a function of Ga content are used to consider the possible trend of the T_0 line describing the equivalence of the free energies of the α and δ phases in the phase diagram. It is suggested that in order to reconcile the need for the existence of a driving force for both the compositionally variant eutectoid reaction, as well as a compositionally invariant martensitic transformation in a Pu—2 at.% Ga alloy, the actual T_0 line may lie higher than that indicated by the present thermodynamical modeling.

Keywords: Actinide alloys and compounds; Phase diagrams; Phase transitions; Solid-state reactions; Thermodynamic properties

1. Introduction

Several papers [1–11] have addressed the Pu–Ga phase diagram, both experimentally and (increasingly) theoretically. Of special interest is the Pu-rich portion, say up to ∼10 at.% Ga. A few details here are still not accurate enough, yet the phase diagram in this range of composition is an important basis for the understanding and interpretation of phase transformations, pre-transformation effects, conditioning of samples, the behavior of martensitic transformations, and the results of various property measurements. The observed behaviors of samples heat treated both above and below the ambient temperature, and particularly if cooled to temperatures well below the ambient, can be often related to the details of the phase diagram.

2. The phase diagram

The most up-to-date information on the Pu–Ga-rich portion of the phase diagram is presented in the well-known publication "A Tale of Two Diagrams" (Fig. 1) [3]. Fig. 1a is based on Ellinger's early work [1] and on subsequent assessment by Peterson and Kassner [8]. These authors refer to Ref. [2], but do not comment on the form of the δ phase field in this diagram, nor the occurrence of the eutectoid reaction. However, the extensions of the phase boundaries of this phase to very low temperatures have been questioned recently and are clearly highly improbable as proposed if one considers the restrictions imposed on solid solubility and phase boundaries by the Nernst Principle and the IIIrd law of thermodynamics (see for example, Abriata and Laughlin [9]). Essentially, because the entropy of mixing is dictated to be zero at 0 K, all random solid solubility is excluded and is reduced to pure elements, or perfectly ordered compounds. There are two possible solutions that conform to the IIIrd law. One can assume that the delta-phase field will progressively narrow and converge to a single point at 0 K corresponding

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doi:10.1016/j.jallcom.2006.09.132

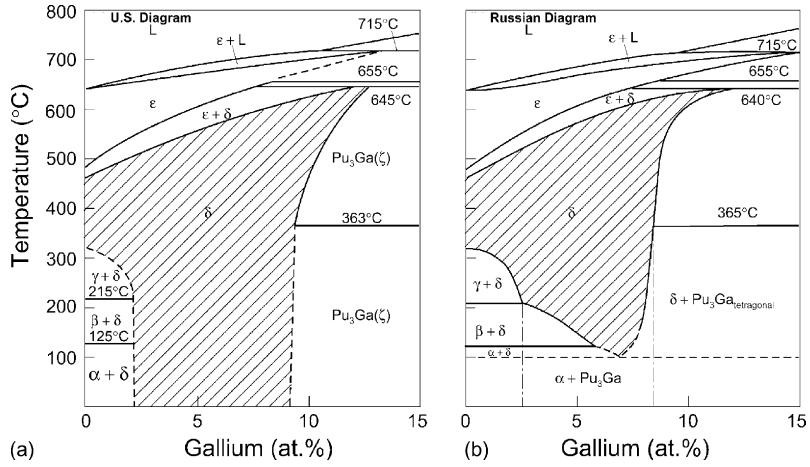


Fig. 1. Phase diagrams as discussed in "A Tale of Two Diagrams" by Hecker and Timofeeva [3]. The phase diagram shown in (a) is considered a "working" phase diagram because the δ phase can be retained to room temperature in a metastable state for extended periods of time. The diagram in (b) exhibits a eutectoid transformation in which the metastable δ phase will decompose to α-Pu and Pu_3Ga.

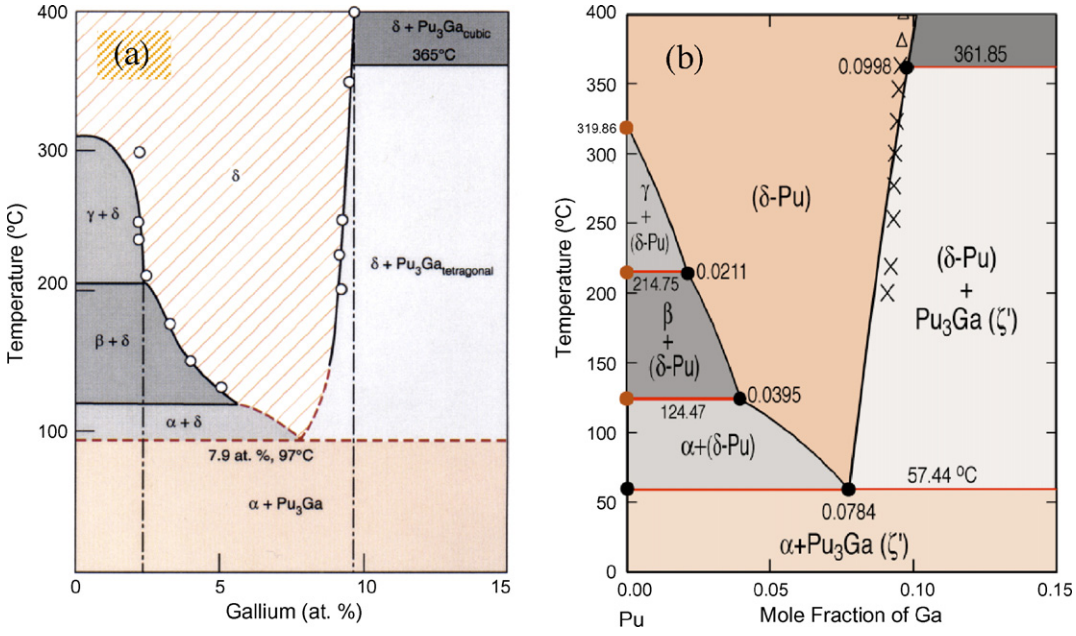


Fig. 2. (a) Proposed equilibrium phase diagram including experimental data points [3,10]. (b) Calculated phase diagram [7] also including experimental data points.

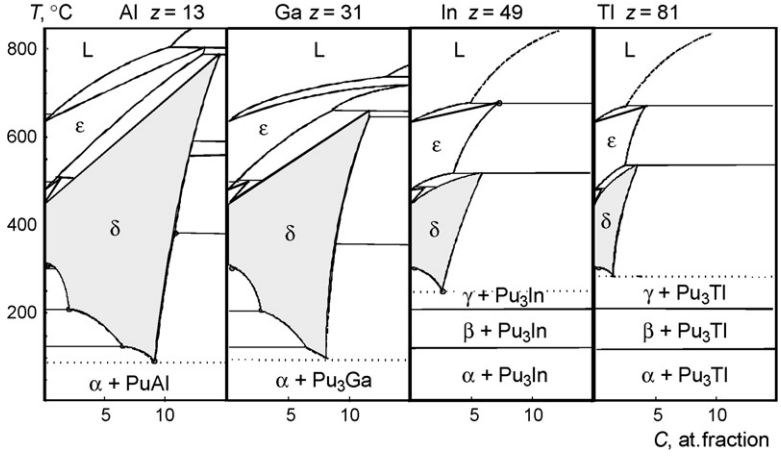


Fig. 3. Proposed phase diagrams of Pu alloys with Al, Ga, In, and Tl [11] illustrating the influence of alloying element on the δ phase stability.

to an ordered compound of appropriate stoichiometry, which is unlikely at these low Ga contents. Hence, a situation involving a eutectoid transformation to pure Pu α phase and Pu_3Ga is to be expected and this indeed is the form of the diagram proposed by the Russian work, as shown in Fig. 1b. The diagram in this figure is mostly based on experimental work in Russia which involved long annealing times at temperatures above about 130 °C, and which also involved ingenious preconditioning of samples and other special treatments such as seeding with the α′ product and prior deformation, all to enhance nucleation and diffusion [10].

As pointed out by Hecker and Timofeeva [3], the form of the diagram in Fig. 1a is currently regarded as a "working" diagram in the range of temperatures near the ambient and the features of the diagram in Fig. 1b essentially represent the current view point of an "equilibrium" phase diagram, although a few minor points may require some correction. The experimental work pertaining to this diagram is based on the data from Chebotarov et al. [2], Timofeeva [10], and others, as indicated by the experimental points in Fig. 2a and b. The experimental work by Chebotarov et al. [2] and Timofeeva [10] in Fig. 2a suggests $X_e = 7.9$ at.% and $T_e = 97$ °C. Both values require some minor extrapolations (see Fig. 2 in red), but they generally conform to other similar eutectoid reactions observed in other Pu systems.

It may be argued that the confirmation of the eutectoid being above the ambient temperature also comes from the systematic trends observed in related Pu systems, particularly with the IIIB elements in the periodic table (Al, Ga, In, and Tl). The trend of the eutectoid reactions is shown in Fig. 3 taken from Timofeeva's paper published in 2003 [11]. It suggests that T_e could be even slightly above 100 °C. Another possible experimental confirmation is from the work of Blobaum et al. on the martensitic transformations in a 2.0 at.% Ga alloy [12]. Interpretation of the results regarding the quantity of the martensitic phase observed on cooling in samples that have been held for several hours of "conditioning" at 25 °C involves the need for a eutectoid reaction temperature to be above 25 °C [12].

Turning now to theoretical work, three different attempts at calculating the phase diagram in the low Ga region have been reported [5–7]. All three calculations confirm the eutectoid reaction $\delta \rightarrow \alpha + Pu_3Ga$ as the feature based on thermodynamic free energy considerations. The diagram calculated by Adler [4,5] utilizing the F.A.C.T. program, is shown in Fig. 4a. As shown in the figure, $T_e = 81$ °C, $X_e = 7.8$ at.% Ga, and the $T_0^{\delta/\alpha}$ temperature for pure Pu, representing the metastable transition temperature between the α and δ phases is at 152 °C. The calculation by Turchi et al. [7], utilizing the CALPHAD approach, is shown in Fig. 4b. This calculation covers the whole phase diagram. The Ga-rich portion is shown in Fig. 3b. It places X_e at 7.84 at.%, but gives the T_e as 57 °C, some 40° below the line proposed in the Russian diagram. The corresponding $T_0^{\delta/\alpha}$ temperature for pure Pu is reported as 157 °C.

Another theoretical confirmation of the eutectoid reaction shown in Fig. 4c comes from the application of molecular dynamics (MD) calculations using the "modified embedded atom method" (MEAM) potential by Baskes et al. [6]. It reproduces the eutectoid, but not all other features. The calculated values $X_e = 1.5$ at.%, and $T_e = 267$ °C (540 K), are substantially

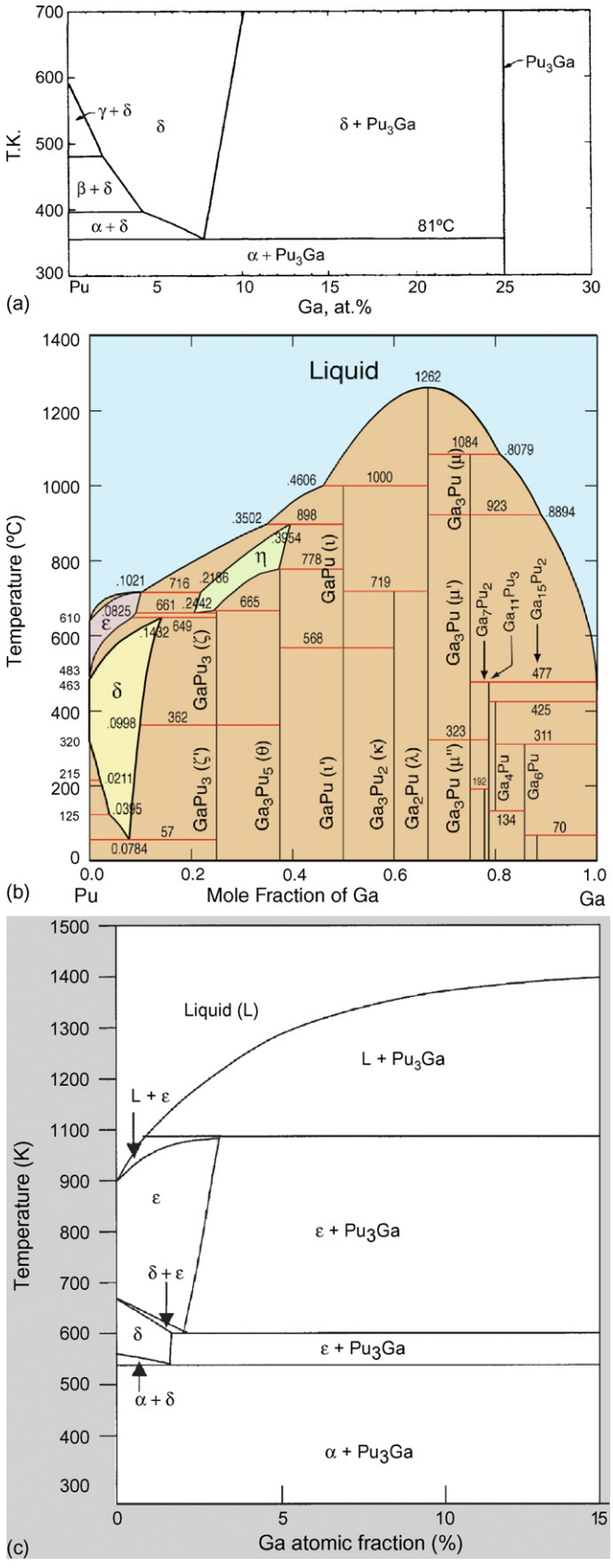


Fig. 4. Calculated phase diagrams by (a) Alder [5] that predicts $T_e = 81$ °C, $X_e = 7.8$ at.% Ga, (b) Turchi et al. [7] that predicts $T_e = 57$ °C, $X_e = 7.84$ at.% Ga, and (c) Baskes et al. [6] that predicts $T_e = 267$ °C, $X_e = 1.5$–1.6 at.% Ga.

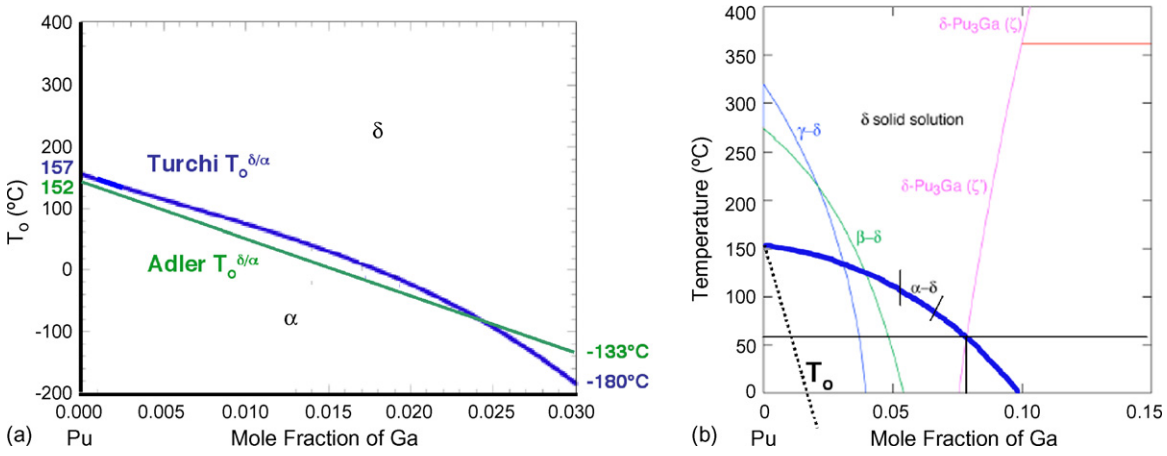
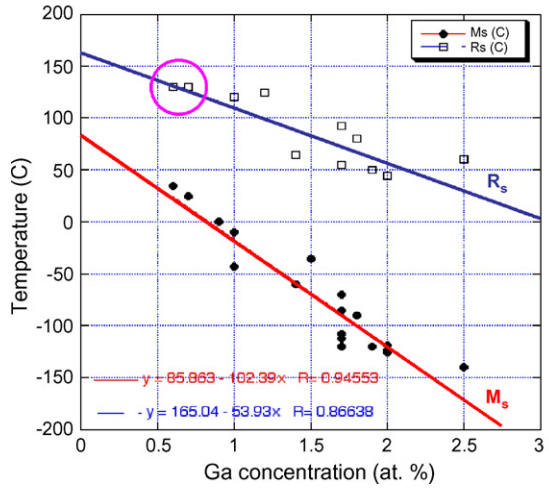


Fig. 5. (a) Calculated $T_0^{\delta/\alpha}$ temperature for the equivalence of free energies between the α and δ phases. (b) Phase boundaries from CALPHAD predictions by Turchi et al. [7]. Also included are the T_0 line and the range of δ phase stability from [3].



at.% Ga	Author	[REF]	M_S (°C)	M_S (K)	R_S (°C)	R_S (K)
0.6	Orme	[14]	35	308	130	403
0.7	Orme	[14]	25	298	130	403
0.9	Faires	[15]	0	273		
1.0	Joel	[16]	-43	230		
1.0	Hecker	[17]	-10	263	120	393
1.2	Deloffre	[18]			125	398
1.4	Orme	[14]	-60	213	65	338
1.5	Faires	[15]	-35	238		
1.7	Joel	[16]	-108	165		
1.7	Adler	[4]	-120	153		
1.7	Adler	[4]	-70	203		
1.7	Mitchell	[19]	-112	161	92	365
1.7	Hecker	[17]	-85	188	55	328
1.8	Hecker	[17]	-90	183	80	353
1.9	Orme	[14]	-120	153	50	323
2.0	Mitchell	[19]	-119	154	44	317
2.0	Mitchell	[19]	-126	151	44	317
2.0	Blobaum	[12]	-123	147	45	318
2.5	Hecker	[17]	-140	133	60	333
3.0	Joel	[16]	None			
3.5	Hecker	[17]	None			

Fig. 6. M_S and R_S temperatures as a function of Ga concentration plotted using data from the literature. See [4,12,14–19].

at variance with the presently accepted values. However, a recent attempt to adjust some of the basic parameters utilized in the calculation lowers the T_e value [13].

The phase diagram calculations by Adler [5] and by Turchi et al. [7] provide also the $T_0^{\delta/\alpha}$ trend (at which the free energies of the two phases are equal) with increasing Ga contents as well as the (α + δ)/δ phase boundary trend, as shown in Fig. 5a. It is of interest to incorporate these trends on the phase diagram itself, to test how they compare with the experimental data derived from the behavior of the martensitic transformations and the extrapolated portion of the relevant δ phase boundary. This is shown in Fig. 5b. Turchi's calculation places the metastable T_0 point at 157 °C on the pure Pu axis and can be used to anchor the proposed (blue line) trend of (α + δ)/δ phase boundary proposed by Hecker and Timofeeva [3] inside the phase diagram. Since there is practically no equilibrium solid solubility of Ga in the monoclinic α phase with a correspondingly very steep free energy curve, it is not surprising that the T_0 line is closer to the α phase boundary (a practically vertical line, not shown) within the two-phase α + δ phase field.

3. The phase diagram and the low temperature phase transformations

Of particular interest to us here are connections between the fine details of the phase diagram and the behavior of the martensitic transformations. To put these transformations into context of the phase diagram it is helpful to include on the phase diagram the likely T_0 trend of the δ → α transformation as discussed above, and also the data on the onset of the martensitic transformation on cooling (M_S trend [1]) and its reversal on heating (R_S trend). Unfortunately, these trends have to be deduced from experimental data obtained from evaluations involving different techniques (for example, DSC, dilatometry, optical microscopy, resistivity, etc.) In each case, the M_S and R_S temperatures are a matter of some judgment because the actually derived values are also affected by the details of each experiment (the cooling

[1] We refer to the onset of the martenstic transformation temperature as M_S. Some authors use M_B to emphasize the burst mode of this transformation.

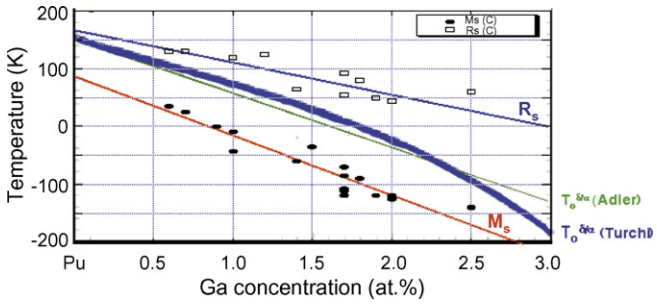


Fig. 7. $T_0^{\delta/\alpha}$ trends by Adler [5], Turchi et al. [7] lie in the mid-space between M_S and R_S.

rate, sample holding time), and the particular samples themselves (composition, homogeneity, grain size, etc.) It has been shown that halving the grain size could lower the M_S by some 40–50 °C [4,17]. The data we have collected on reported M_S and R_S temperatures is listed in the table accompanying Fig. 6 which also shows the resulting trends with Ga concentration.

It is considerably more difficult to derive the reversal R_S trend as a function of composition. As already pointed out by Hecker et al. [17] and Deloffre et al. [18], as the Ga content decreases the reversal process may involve sequences whereby α' reverts initially (at least partially) to the β phase, i.e., $\alpha \rightarrow \beta \rightarrow \gamma$, typical of the unalloyed Pu. Hence, it is more difficult to judge the R_S ($\alpha' \rightarrow \delta$) temperatures from the reversal trends of property changes, such as DSC, or dilatometry. The few available temperature/composition points in the low Ga range appear to have very similar values as circled in Fig. 6. A comparison between the calculated $T_0^{\delta/\alpha}$ trends and the trends of M_S and R_S temperatures is shown in Fig. 7. As expected, T_0 falls within the mid-space between R_S and M_S although is may be somewhat closer to R_S in lower Ga alloys and closer to M_S at higher values.

It is reasonable that the T_0 should not be considered a mean value of M_S and R_S [$(M_S + R_S)/2$] as initially proposed by Adler [5], because the reversal process does not involve nucleation [12] and hence the R_S trend may be less displaced upwards from T_0 than the downward displacement of the M_S from T_0 as shown as the proposed T_0 line in Fig. 8.

The connections between the phase diagram, the T_0, and the M_S and R_S transformation temperatures associated with the martensitic transformations, as they apply to an alloy of a particular composition of approximately 1.9 at.% Ga, can be now considered in terms of a diagram such as that in Fig. 8. Here, we also include some data on the well-known double-C plot obtained in earlier studies of low temperature time–temperature–transformation (TTT) diagrams for an alloy of approximately 1.9 at.% Ga [14]. The composition line for this alloy cuts the calculated T_0 trends at −20 °C, which therefore provides some 100 °C undercooling to drive the martensitic transformation $\delta \rightarrow \alpha'$ at the onset of the upper-C transformations at about −120 °C. The lower C initiating below about −145 °C corresponds in this context to about −125 °C undercooling below T_0 and hence involves a somewhat larger driving force for this isothermal mode. Perhaps, because of this, the incubation time prior to the martensitic burst at the lower C temperature is somewhat shorter than at the upper C. Both driving energy values could be estimated, in principle, from the modeling calculations, which provide free energy trends.

Of particular interest in Fig. 8 is the need to provide sufficient driving force at the nucleation stage (presumably to a large degree at 25 °C), prior to the actual occurrence of the martensitic bursts within the δ matrix that characterize the martensitic transformation at M_S temperatures, and below. Since the individual martensitic units appear to form in a heterogeneous manner in the matrix, they must be associated with some pre-existing nucleation sites, which become activated on cooling. In a recent study of a 2 at.% Ga alloy, Blobaum et al. [12] postulate the formation of initially composition-invariant α embryos during the conditioning at 25 °C for a few hours, which subsequently burst into martensite particles on cooling to the cryogenic temperature range (see Fig. 8). Since the conditioning temperature is some

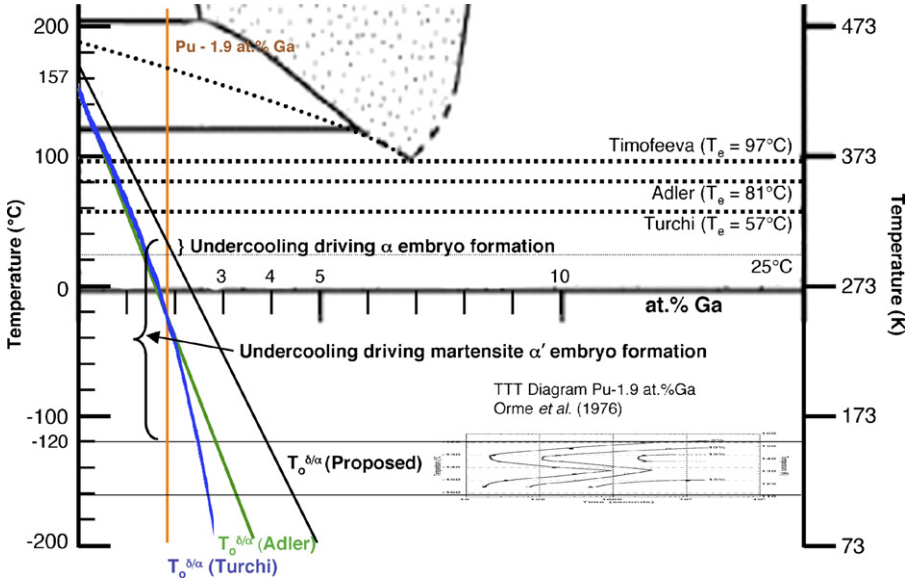


Fig. 8. $T_0^{\delta/\alpha}$ lines plotted on the Hecker and Timofeeva [3] phase diagram. The proposed $T_0^{\delta/\alpha}$ line crosses the Pu–1.9 at.% Ga alloy above room temperature.

75 °C below the eutectoid there is, in principle, considerable driving force for the initial stages of a eutectoid reaction. However, if these embryos have initially the same composition as the δ matrix (i.e., an average composition of 2 at.% Ga), the undercooling below the corresponding T_0 is only very slight, unless the T_0 line is turned upwards, or shifted, (as proposed in Fig. 8) to provide more undercooling. Thus, if the formation of possible embryos is related to free energy considerations between the competing phases, the fine details of the phase diagram, the thermodynamics, and the phase transformations that occur in the metastable range of the delta phase are clearly interrelated.

Acknowledgment

This work was performed under the auspices of the US Department of Energy by University of California Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48.

References

[1] F.H. Ellinger, C.C. Land, V.O. Struebing, J. Nucl. Mater. 12 (2) (1964) 226.
[2] N.T. Chebotarev, E.S. Smotriskaya, M.A. Andrianov, O.E. Kostyuk, Plutonium 1975 and Other Actinides, in: H. Blank, R. Lindner (Eds.), Amsterdam, 1975, pp. 37–46.
[3] S.S. Hecker, L.F. Timofeeva, Los Alamos Sci. 26 (2000) 244.
[4] P.H. Adler, G.B. Olson, Metall. Trans. 19A (1988) 2705.
[5] P.H. Adler, Metall. Trans. 22A (1991) 2237.
[6] M.I. Baskes, K. Muralidharan, M. Stan, S.M. Valone, F.J. Cherne, JOM 55 (9) (2003) 41.
[7] P.E.A. Turchi, L. Kaufman, Z.-K. Liu, S. Zhou, UCRL-TR-206658, 2004.
[8] T.B. Massalski, H. Okamoto, L. Kacprzak, Binary Alloy Phase Diagrams, second ed., American Society for Metals, 1990.
[9] J.P. Abriata, D.E. Laughlin, Prog. Mater. Sci. 49 (2004) 367.
[10] L.F. Timofeeva, Ageing Studies and Lifetime Extension of Materials, in: L.G. Mallinson (Ed.), New York, 2001, pp. 191–198.
[11] L.F. Timofeeva, Atom. Energy 95 (2) (2003) 540.
[12] K.J.M. Blobaum, C.R. Krenn, M.A. Wall, T.B. Massalski, A.J. Schwartz, Acta Mater. 54 (2006) 4001.
[13] M. Stan, Private communication, 2006.
[14] J.T. Orme, M.E. Faiers, B.J. Ward, Plutonium 1975 and Other Actinides, in: H. Blank, R. Lindner (Eds.), Amsterdam, 1975, p. 761.
[15] M.E. Faiers, R.G. Loasby, B.J. Ward, J.T. Orme, B.R. Spicer, in: A.E. Kay, M.B. Waldron (Eds.), Third International Conference on Plutonium, London, 1965, p. 64.
[16] J. Joel, C. Roux, M. Rapin, J. Nucl. Mater. 40 (1971) 297.
[17] S.S. Hecker, D.R. Harbur, T.G. Zocco, Prog. Mater. Sci. 49 (2004) 429–485.
[18] P. Deloffre, J.L. Truffier, A. Falanga, J. Alloy. Compound. 271–273 (1998) 370.
[19] J.N. Mitchell, M. Stan, D.S. Schwartz, C.J. Boehlert, Met. Trans. 35A (2004) 2267.